

p -type conductivity in $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ films and powders

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$\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$, a wide band gap semiconductor with the delafossite structure, has been synthesized in bulk and thin-film form. Bulk undoped CuCrO_2 is almost black and has moderate conductivity with p -type carriers. Upon doping with 5% Mg, the conductivity increases by a factor of 1000. In films, the best p -type conductivity is 220 S cm^{-1} in $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$, a factor of 7 higher than previously reported for Cu-based p -type delafossites. Undoped films have a conductivity of order 1 S cm^{-1} . Films are usually polycrystalline on amorphous substrates, but undoped films can be c -axis oriented if deposited at or above 650°C . Optical and ultraviolet transmission data indicate a direct band gap of 3.1 eV . © 2001 American Institute of Physics. [DOI: 10.1063/1.1372636]

INTRODUCTION

The CuMO_2 class of materials,¹ where M is a trivalent cation, has the delafossite structure shown in Fig. 1. This group has been of renewed interest since Kawazoe *et al.* reported p -type conductivity in a transparent thin film of CuAlO_2 .² Although the conductivity was several orders of magnitude lower than that of the more commonly used transparent conducting oxides (TCOs) like ZnO_{1-x} , $\text{In}_{1-x}\text{Sn}_x\text{O}_3$, and Cd_2SnO_4 , the fact that the conductivity was p type, in contrast to the n -type conductivity of the latter compounds, fueled hopes that transparent electronics might be feasible.³ Reports followed of films of similar p -type delafossite TCOs like CuScO_2 ,⁴ CuGaO_2 ,⁵ and $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$ (Ref. 6) with the highest reported p -type conductivity being 30 S cm^{-1} in a CuScO_2 thin film. The potential of these materials as device elements is beginning to be demonstrated with reports of rectifying pn diodes based on SrCu_2O_7 ,⁷ and on $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$,⁶ and light-emitting diodes.⁸ In this article, we report significantly higher conductivity in thin films of $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$. This report is interesting because it may indicate that the particular cation on the octahedral site is indeed important for conductivity. Cr^{3+} is also distinct from Y^{3+} , Sc^{3+} , Al^{3+} , Ga^{3+} , or In^{3+} in that $d-d$ transitions are possible, and we do find that the transparency is lower than in $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$ or $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$ films.

While potential applications of transparent conductive oxides will undoubtedly come from thin films, much of the basic chemistry and physics is more easily studied in the

bulk form of the material. To this end, we have also studied resistivity and analyzed x-ray diffraction patterns of powdered $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$.

CuCrO_2 has been synthesized and studied in powder and single crystal form (CuCrO_2 is used as catalyst to extract CO and hydrocarbons from the exhausts of various burn reactions), but there are, to our knowledge, no reports of thin films.

MATERIALS PREPARATION

Bulk $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ was prepared using appropriate quantities of CuO (Cerac Pure 99.9%), Cr_2O_3 (Baker analyzed), and MgO (Aldrich 99+%). The starting components were thoroughly ground together in an agate mortar and pestle. The resultant mixture was then pressed to form a pellet, which was sintered at 1200°C for 48 h and quenched in air.⁹

Thin films were prepared by on-axis rf sputtering at 90 W of a 5 cm diameter target of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$. The base pressure in the chamber was $7-10^{-6}$ Torr, and 5N-Ar at 10 mTorr was the sputter gas. The target was presputtered before each deposition to remove surface contaminants. Fused quartz substrates were attached to a Neocera heater using silver paint to ensure good thermal contact, and placed 3.8 cm from the surface of the target. Deposition temperatures between 450 and 750°C ensured good film adhesion and reasonable deposition rates of $5-10 \text{ nm/min}$. Films were typically $200-300 \text{ nm}$ thick as measured by a stylus profilometer (Tencor Instruments Alpha-Step 100), but occasionally were much thinner or thicker for special purposes. Following

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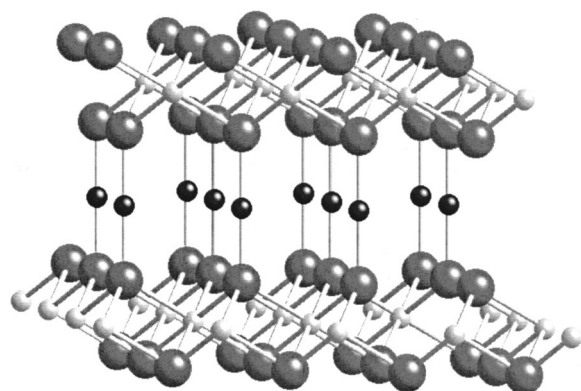


FIG. 1. CuMO_2 in the delafossite structure has Cu (small dark spheres) coordinated to two oxygen atoms (large dark spheres) and M (small light spheres) coordinated to six oxygen atoms.

deposition the heater was turned off and the films were allowed to cool to room temperature. Postprocessing of some samples was by rapid thermal annealing (RTA) in a flowing argon atmosphere with an AET RX rapid thermal annealer. The entire RTA procedure took less than 15 min and the samples were maintained at the desired temperature (600–900 °C) for about 2.5 min. RTA at 900 °C was useful in inducing higher transparency in the films, at the expense of conductivity and sometimes film uniformity. Oxygen proved to be detrimental by introducing the CuCr_2O_4 phase.

STRUCTURAL PROPERTIES

An atomic force microscope (Digital Instruments NanoScope III) was used to determine surface roughness of two Mg-doped CuCrO_2 films produced in the same deposition. Analysis showed a root mean square roughness of 12.8 nm over a 2 square micron area for an as-deposited film, and 38.6 nm for the film subjected to 900 °C RTA. Grain size increased from 10 nm to 0.7 μm under this treatment.

Wavelength-dispersive electron probe microanalysis (EPMA) indicated that the bulk material had Cu:Cr:Mg stoichiometry consistent with the compositions of the starting reactants. Rutherford backscattering spectroscopy analysis showed that the films have a Cu:Cr ratio about 10% higher than the bulk material from which the sputter target was made. Mg was found at the limit of detection, which is consistent with target stoichiometry. EPMA on the films confirmed the Cu-rich conclusion, and quantitatively established the Cu:Mg ratio as that of the target.

The crystal structure was examined by x-ray diffraction (XRD) in the θ - 2θ geometry using a Siemens D-5000 spectrometer. This is primarily a powder spectrometer, but is also very useful for strongly oriented films. For polycrystalline or weakly crystalline films, we used an INEL diffractometer whose rotating anode and position sensitive detector allow much higher count rates. The bulk material is monophasic, possessing the 3R delafossite structure, for all the Mg concentrations from 0% to 5%. The absence of the 2H polytype implies that the cooling rate is slow enough to inhibit formation of this metastable form. This is consistent with the observations of Crottaz *et al.*,¹⁰ who reported single crystals of

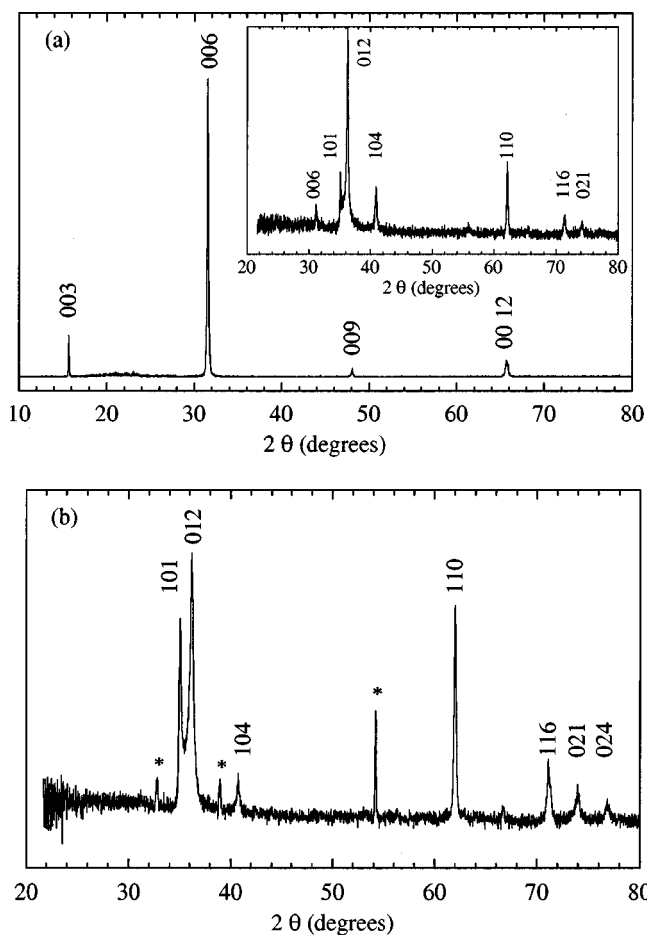


FIG. 2. X-ray diffraction patterns of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ thin films on amorphous quartz. (a) Undoped CuCrO_2 . The main panel shows the c -axis orientation of the film, which was deposited at 650 °C. The inset shows a film deposited at 550 °C and annealed in Ar at 900 °C. The film is polycrystalline and is the 3R polytype. (b) $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$ deposited at 600 °C. It is also a polycrystalline version of the 3R polytype. The small peaks marked “*” are from In contacts. The polycrystalline spectra have the amorphous substrate background subtracted.

2H-CuCrO_2 obtained by rapidly quenching 3R- CuCrO_2 crystals from 1100 °C, but were unable to obtain phase-pure 2H powders. Our attempts to intercalate oxygen to form CuCrO_{2+x} were not successful. There was no oxygen uptake in air at any temperature, or in oxygen at low temperature as determined by thermogravimetric analysis. Soaking CuCrO_2 in oxygen above 1200 °C produced CuCr_2O_4 . CuAlO_2 is similarly difficult to intercalate, but CuScO_2 takes up oxygen quite readily.

The XRD patterns of the films led to the following general observations. Undoped CuCrO_2 films deposited on fused quartz between 150 and 650 °C were amorphous, but became polycrystalline after RTA in Ar, without a significant change in resistivity. The XRD pattern is shown in the inset to Fig. 2(a). Above a deposition temperature of 650 °C, undoped films were c -axis oriented as deposited, as shown in Fig. 2(a) where the (00 l) reflections are very strong. Mg-doped CuCrO_2 films deposited at substrate temperatures between 400 and 700 °C were polycrystalline as deposited [Fig. 2(b)] and the crystallinity was not significantly improved by annealing. We never obtained strongly oriented films of the

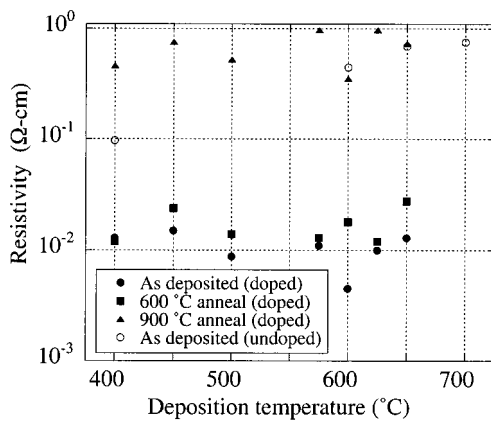


FIG. 3. Dependence of film resistivity on substrate temperature at deposition. The as-deposited doped films (solid circles) are more conducting before they are annealed (solid squares, triangles), and are more conducting by about a factor of 100 than undoped films (open circles) prepared under the same conditions.

doped material, and doped films deposited at temperatures lower than 400 °C did not adhere.

ELECTRICAL PROPERTIES

The dc resistivity was measured with an in-line four-point probe configuration and sometimes in a van der Pauw configuration for films. The carrier type was established by measurement of the Seebeck voltage induced by a temperature gradient. The resistance of the bulk material dropped by a factor of 1000 as a result of the Mg doping, and encouraged us to pursue thin film synthesis. This decrease is about the same as observed for Ca doping of CuYO_2 ,¹¹ and roughly an order of magnitude larger than we have observed for Mg doping of CuScO_2 . Similar attempts by us and others to dope CuAlO_2 and CuGaO_2 have been unsuccessful.

The *p*-type conductivity in bulk and thin-film $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ must be strongly driven by the divalent cation doping on the trivalent site, but it is not clear why the “undoped” material is conductive. Holes cannot be introduced by oxygen intercalation, since attempts to do this simply resulted in the formation of CuCr_2O_4 . We also prepared Cu-deficient material ($\text{Cu}_{0.9}\text{Cr}_{1.0}\text{O}_2$) to see whether Cu vacancies might play a role. We conclude not, because the Cu-deficient material was dark green and insulating. Cu-rich material ($\text{Cu}_{1.1}\text{Cr}_{0.9}\text{O}_2$) was prepared in the same manner to see whether Cu^{2+} would occupy the octahedral site as it does in the double delafossite $\text{Cu}_2\text{CuTiO}_4$. The result was inconclusive because XRD revealed a mixture of CuCrO_2 and CuO .

Measurements of the effect on film resistivity of substrate temperature during film deposition are summarized in Fig. 3. Undoped CuCrO_2 films as deposited on amorphous quartz between 400 and 700 °C had a resistivity slightly less than about 1 Ω cm. Films doped with 5% Mg deposited under the same conditions had much lower as-deposited resistivities, typically about 0.01 Ω cm. The lowest we observed was 0.045 Ω cm, corresponding to a conductivity of 220 S cm^{-1} . The transparency of such films about 250 nm thick was about 30% in the visible range. Postannealing at 600 °C did not significantly alter the resistivity, crystallinity, or the

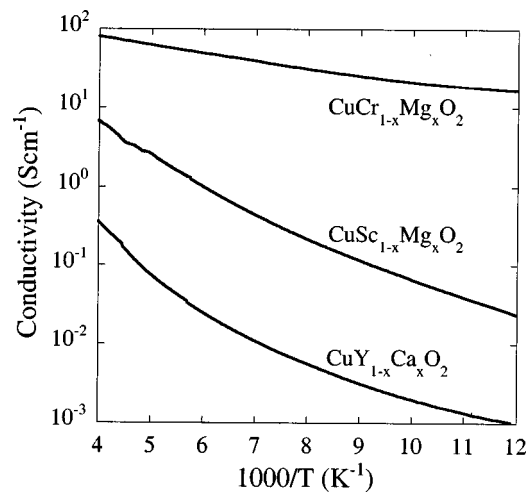


FIG. 4. Temperature dependence of the conductivity of films of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$, $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$, and $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$.

transparency, but postannealing at 900 °C improved the transparency to about 40% and increased the resistivity to about 1 Ω cm. For comparison, we note a recent report of similar thickness CuAlO_2 films with 70% transparency in the visible and resistivity about around 0.3 S cm^{-1} .¹²

The temperature dependence of the dc resistivity of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ films shows semiconductor-like behavior, decreasing with increasing temperature. However, the change in resistivity between room temperature and 77 K is less than a factor of ten, significantly smaller than for other delafossites we have measured. This is illustrated in the conductivity plot in Fig. 4. The plots of $\log \sigma$ versus $1000/T$ for $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$, $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$, and $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$ films are approximately linear from 160–300 K, yielding activation energies of 20, 95, and 130 meV, respectively, although one should be cautious about extracting an “activation energy” from a relatively small change in conductivity ($\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$). At lower temperatures a fit to $\log \sigma$ versus $1/T^{1/4}$, the variable range hopping model, is better for the less conductive materials. The increasing conductivity tracks a decreasing ionic radius of the M^{3+} cation, and decreasing lattice parameter in the plane of the Cu atoms. This suggests increased overlap between Cu *d* orbitals and better charge mobility. There are no comparative band structure calculations that could address to what extent the *d* orbitals of the different M cations might influence the valence band structure and account for the conductivity trend.

Thermopower measurements established the conductivity of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ powders and films as *p* type, with a Seebeck coefficient of 150 $\mu\text{V/K}$ for the films. This is much lower than the 1210 $\mu\text{V/K}$ reported by Benko and Koffyberg (BK) for bulk powdered samples of Ca-doped CuCrO_2 .¹³ The resistivity of their material (100 Ω cm) was much higher than that of the films we measured (0.01 Ω cm). If we use the small polaron hopping model employed by BK, namely

$$S = \frac{k_b}{e} \ln \left(\frac{N_0}{N_A} \right)$$

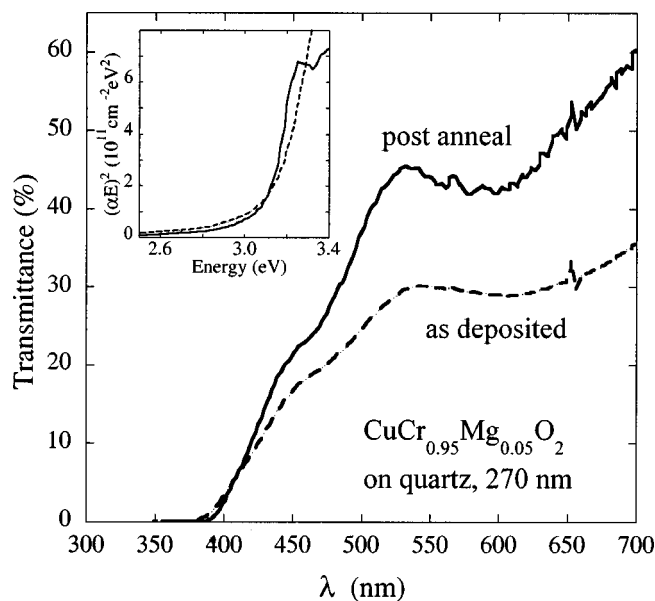


FIG. 5. Optical transmittance data for films of $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$ showing that improved transparency results from annealing. The conductivity of the as-deposited film is 100 S cm^{-1} , and that of the post annealed film is 1 S cm^{-1} . The inset shows $(\alpha E)^2$ vs photon energy E , yielding a direct gap of 3.1 eV.

to calculate a carrier density from the thermopower, we obtain for the ratio of the number of carriers to the number of Cu^+ ions N_A/N_0 , a value of 17%. This is at least of the same order as the 5% Mg doping level, but the agreement is obviously not quantitative. Further, this would predict a mobility of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or lower for our films. Hall measurements in a van der Pauw configuration did not yield carrier type at room temperature, which puts an upper limit on the room-temperature carrier mobility of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a simple single-band model.

OPTICAL PROPERTIES

The transmittance of films in the wavelength range 190–820 nm was measured with a diode array spectrophotometer (UV–VIS HP 8452A). The optical transmission spectra of a 300 nm $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$ film, as deposited and after annealing, are shown in Fig. 5. This example is typical—films were more transparent after they had been subjected to RTA in argon. However, the overall transparency remained relatively low. Estimates of the size of the band gap were obtained by extracting the absorption coefficient α and plotting $(\alpha h\nu)^n$ vs $h\nu$.¹⁴ The strongest change in absorption yielded a gap energy E_g of 3.10 eV with $n=2$ (direct gap) for both the as-deposited and annealed film. Photoelectrochemical mea-

surements by BK¹³ gave $3.08 \pm 0.3 \text{ eV}$ and indicated an indirect gap. Our data were better fit to the direct gap assumption, but the analysis performed assuming an indirect gap gave a value of 2.75 eV. BK also reported an indirect gap at 1.28 eV, and a direct gap at 3.35 eV. We see some structure in the absorption that could be consistent with an indirect gap at about 1.45 eV and possibly a further direct gap of about 2.35 eV.

We have shown that very good *p*-type conductivity is induced in bulk $3\text{R}-\text{CuCrO}_2$ by substitution of Mg for Cr, and not by oxygen intercalation. Films prepared from phase pure sputter targets have shown the highest *p*-type conductivity of any delafossite films to date, and the temperature dependence of the conductivity is much weaker than for other CuMO_2 delafossites. Films can be amorphous, polycrystalline, or oriented depending on the substrate, its temperature, and the postdeposition processing. The optical transmission spectra are consistent with a direct band gap of 3.1 eV. Optical transmittance is in the range of 30%–40% near 500 nm, and the conductivity is reduced from 200 to about 1 S cm^{-1} to improve transparency.

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